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(71) Applicant (for all designated States except US): **SHELL OIL COMPANY** [US/US]; One Shell Plaza, P.O. Box 2463, Houston, TX 77252-2463 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **DUONG, Dien, Hien** [US/US]; 16210 Canario, Houston, TX 77083 (US). **LU, Jian** [US/US]; 14211 Highcroft Avenue, Houston, TX 77077 (US). **VI, Nga, Thihuyen** [US/US]; 20731 Lariat Canyon Drive, Katy, TX 77450 (US).

(74) Agent: **LEMUTH, Richard, F.**; SHELL OIL COMPANY, One Shell Plaza, P.O. Box 2463, Houston, TX 77252-2463 (US).

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(54) Title: A METHOD OF PREPARING A SHAPED CATALYST, THE CATALYST, AND USE OF THE CATALYST

(57) Abstract: A method of preparing a shaped catalyst, which method comprises moulding a dough into shaped particles and drying at least a portion of the shaped particles at a temperature below 1000°C, wherein the dough comprises a support material, or a precursor thereof, and a silver component; the shaped catalyst, and a use of the shaped catalyst.



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A METHOD OF PREPARING A SHAPED CATALYST,
THE CATALYST, AND USE OF THE CATALYST

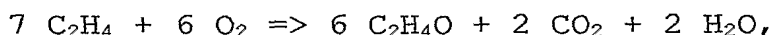
5 Field of the Invention

The invention relates to a method of preparing a shaped catalyst, and a shaped catalyst which is obtainable by the method. The invention also relates to a process for the epoxidation of an olefin, which process comprises contacting
10 a feed comprising the olefin and oxygen with the shaped catalyst. The invention also relates to a method of using the olefin oxide so produced for making a 1,2-diol, a 1,2-diol ether or an alkanolamine.

Background of the Invention

15 In olefin epoxidation an olefin is reacted with oxygen in the presence of a silver-based catalyst to form the olefin epoxide. The olefin oxide may be reacted with water, an alcohol or an amine to form a 1,2-diol, a 1,2-diol ether or an alkanolamine. Thus, 1,2-diols, 1,2-diol ethers and
20 alkanolamines may be produced in a multi-step process comprising olefin epoxidation and converting the formed olefin oxide with water, an alcohol or an amine.

Conventional silver-based catalysts have provided the olefin oxide notoriously in a low selectivity. For example,
25 when using a conventional catalyst, the selectivity towards ethylene oxide, expressed as a fraction of the ethylene converted, does not reach values above the 6/7 or 85.7 mole-% limit. Therefore, this limit has long been considered to be the theoretically maximal selectivity of this reaction, based
30 on the stoichiometry of the reaction equation



cf. Kirk-Othmer's *Encyclopedia of Chemical Technology*, 3rd ed., Vol. 9, 1980, p. 445.

The catalysts are also subject to an aging-related performance decline during normal operation. The aging manifests itself by a reduction in the activity of the catalyst. Usually, when a reduction in activity of the catalyst is manifest, the reaction temperature is increased in order to compensate for the reduction in activity. The reaction temperature may be increased until it becomes undesirably high, at which point in time the catalyst is deemed to be at the end of its lifetime and would need to be exchanged.

Generally, the commercially applied olefin epoxidation catalysts are shaped catalysts which comprise silver deposited on a support. They are prepared by a method which involves impregnating or coating the shaped support with a solution comprising a silver component. The support is commonly prepared by moulding a dough comprising the support material or a precursor thereof into shaped particles and drying the particles at a high temperature of, for example, at least 1000 °C. Numerous patent publications disclose examples of such catalyst preparation.

Over the years much effort has been devoted to improving olefin epoxidation catalysts in their performance, for example in respect of their initial activity and selectivity, and in respect of their stability performance, that is their resistance against the aging-related performance decline. Solutions have been found in improved compositions of the catalysts, and, in other instances, solutions have been found in improved processes of preparing the catalysts.

Modern silver-based catalysts are more selective towards olefin oxide production. When using the modern catalysts in the epoxidation of ethylene the selectivity towards ethylene oxide can reach values above the 6/7 or 85.7 mole-% limit referred to hereinbefore. Such high-selectivity catalysts

may comprise as their active components silver, and one or more high-selectivity dopants, such as components comprising rhenium, tungsten, chromium or molybdenum. High-selectivity catalysts are disclosed, for example, in US-A-4761394 and US-
5 A-4766105.

In respect of improved processes of preparing the catalysts, for example, US-B-6368998, which is incorporated herein by reference, shows that washing the support with water, prior to the deposition of silver, leads to catalysts
10 which have improved initial performance properties.

It goes without saying that -despite the many improvements already seen- it remains highly desirable to improve the performance of olefin epoxidation catalysts, in respect of one or more of their activity, selectivity and
15 stability.

Summary of the invention

The invention provides a method of preparing a shaped catalyst, which method comprises moulding a dough into shaped particles and drying at least a portion of the shaped
20 particles at a temperature below 1000 °C, wherein the dough comprises a support material, or a precursor thereof, and a silver component.

The invention also provides a shaped catalyst which is obtainable by the method in accordance with this invention.

25 The invention also provides a process for the epoxidation of an olefin, which process comprises contacting a feed comprising the olefin and oxygen with a shaped catalyst which is obtainable by the method in accordance with this invention.

30 The invention also provides a method of using an olefin oxide for making a 1,2-diol, a 1,2-diol ether or an alkanolamine comprising converting an olefin oxide into the 1,2-diol, the 1,2-diol ether, or the alkanolamine, wherein

the olefin oxide has been obtained by a process for the epoxidation of an olefin in accordance with this invention.

Detailed Description of the Invention

Catalysts prepared in accordance with this invention can exhibit unexpectedly an improved performance in olefin epoxidation relative to catalysts prepared from the same materials, wherein however the silver component is deposited on an already shaped support. The improved performance is apparent from one or more of an improved initial activity, improved initial selectivity, improved activity stability and improved selectivity stability. Initial selectivity is meant to be the maximum selectivity which is achieved in the initial phase of the use of the catalyst wherein the catalysts slowly but steadily exhibits an increasing selectivity until the selectivity approaches a maximum selectivity, which is termed the initial selectivity. The initial selectivity is usually reached before a cumulative olefin oxide production over the catalyst bed has amounted to, for example, 0.2 kTon/m³ of catalyst bed or 0.15 kTon/m³ of catalyst bed, in particular to 0.1 kTon/m³ of catalyst bed. The invention provides as an advantage that less process steps are involved in preparing a shaped catalyst starting from a particulate carrier material than in the case a particulate carrier material is first shaped and the shaped carrier particles are provided with catalytically active materials. It is also unexpected that, although the carrier material is not exposed to very high temperatures when the shaped particles are dried, the shape catalyst has nevertheless appreciable crush strength.

The support material for use in this invention may be natural or artificial inorganic particulate materials and they may include refractory materials, silicon carbide, clays, zeolites, charcoal and alkaline earth metal

carbonates, for example calcium carbonate or magnesium carbonate. Preferred are refractory materials, such as alumina, magnesia, zirconia and silica. The most preferred material is α -alumina. Typically, the support material
5 comprises at least 85 %w, more typically 90 %w, in particular 95 %w α -alumina or a precursor thereof, frequently up to 99.9 %w, or even up to 100 %w, α -alumina or a precursor thereof. The α -alumina may be obtained by mineralization of α -alumina, suitably by boron or, preferably, fluoride
10 mineralization. Fluoride mineralized α -alumina may be of a platelet structure. A preferred α -alumina is of such platelet structure. Reference is made to US-A-3950507, US-A-4379134 and US-A-4994589, which are incorporated herein by reference.

15 Precursors of support materials may be chosen from a wide range. For example, α -alumina precursors include hydrated aluminas, such as boehmite, pseudoboehmite, and gibbsite, as well as transition aluminas, such as the chi, kappa, gamma, delta, theta, and eta aluminas.

20 The support material or precursor thereof may be a particulate material which may have any particle size distribution. The particle size distribution may be monomodal, or multimodal, for example bimodal or trimodal. Typically, the particle size distribution is such that the
25 particulates have a d_{50} of at least 0.1 μm , more typically at least 0.2 μm , in particular at least 0.5 μm , more in particular at least 1 μm . Typically, the particle size distribution is such that the particulates have a d_{50} of at most 100 μm , more typically at most 80 μm , in particular at
30 most 50 μm , more in particular at most 20 μm . Typically, from 80 to 100 %w of the particles has a particle size within the range of from 10 to 1000 % of the d_{50} value of the particle size distribution. In particular, from 80 to 100 %w

of the particles has a particle size within the range of from 20 to 600 % of the d_{50} value of the particle size distribution. The average particle size, referred to herein as " d_{50} ", is as measured by a Cilas laser particle size analyzer and represents a particle diameter at which there are equal spherical equivalent volumes of particles larger and particles smaller than the stated average particle size.

In one embodiment, the support material or precursor thereof may be a mixture of particulate materials of different particle sizes. In particular, the support material may be a mixture containing (1) one or more particulate materials comprising particulates having a d_{50} of at most 3 μm , typically at most 1 μm in a quantity of at least 1 %w, typically at least 5 %w, and more typically in the range of from 10 to 20 %w, relative to the weight of the support material or precursor thereof; and (2) one or more particulate materials comprising particulates having a d_{50} of more than 3 μm , typically at least 5 μm in a quantity of at most 99 %w, typically at most 95 %w, and more typically in the range of from 80 to 90 %w, relative to the weight of the support material or precursor thereof. The effect of having the smaller particles in the support material together with the larger particles is an improvement in the activity and/or the mechanical strength of the shaped catalyst. This effect may be achieved independent of whether the shaped particles are dried at a temperature below 1000 °C, or at 1000 °C or above.

The support material or precursor thereof may typically have a surface area in the range of from 0.1 to 5 m^2/g , more typically from 0.2 to 2 m^2/g , in particular from 0.5 to 1.5 m^2/g . "Surface area" as used herein is understood to refer to the surface area as determined by the BET (Brunauer,

Emmett and Teller) method as described in Journal of the American Chemical Society 60 (1938) pp. 309-316.

Commercially available α -aluminas useful in the process of the invention include, but are not limited to, the following types: A 20 SG, A 3500 SG, A 10-325, A 14-325, A2-325, CT 800 SG, CL 2500 SG, and CL 3000 FG, available from Alcoa World Chemicals/Almatis Inc.; APA-0.5, SPA-TMXX3 and APA-8 AF, available from Sasol North America Inc.; and AC34B4, AC44B4, P122, P122B, P122SB, and P662B, available from Altech/Alcan Inc.

A bond material may or may not be incorporated into the dough. The bond material is a material which facilitates bonding the particles of the support material or precursor thereof together. The bond material also may form a coating on at least a part of the support surface, which makes the support surface more receptive.

In particular when the support material is α -alumina, the bond material may typically be based on a silica-containing composition, for example, a silica sol, a precipitated silica, an amorphous silica, or an amorphous alkali metal silicate, alkaline earth metal silicate or aluminasilicate. Typically, the silica-containing compositions for use as a bond material may also comprise hydrated alumina and/or an alkali metal salt, such as a carbonate, bicarbonate, formate, acetate, nitrate, or sulfate. Typically, the alkali metal is lithium, sodium, or potassium, or a combination thereof.

In advantageous embodiments, the support material or precursor thereof may have been treated, in particular in order to reduce its ability to release sodium ions, i.e. to reduce its sodium solubilization rate, or to decrease its content of water soluble silicates. A suitable treatment comprises washing with water. For example, the support

material or precursor thereof may be washed in a continuous or batch fashion with hot, demineralised water, for example, until the electrical conductivity of the effluent water does not further decrease, or until in the effluent the content of sodium or silicate has become very low. A suitable temperature of the demineralised water is in the range of 80 to 100 °C, for example 90 °C or 95 °C. Alternatively, the support material or precursor thereof may be washed with base and subsequently with water. After washing, the support material or precursor thereof may typically be dried. Reference may be made to US-B-6368998, which is incorporated herein by reference. Catalysts which have been prepared by using the support material or precursor material that has been so treated have an improved performance in terms of an improved initial activity, initial activity and/or selectivity stability.

The dough comprises a silver component. The silver component may be dispersed metallic silver, or alternatively the silver component may comprise a compound of cationic silver. Cationic silver may be reduced to metallic silver at any stage of the catalyst preparation, for example during the drying of the shaped particles or in a subsequent step. Reducing agents may be included in the dough, which effect reduction of cationic silver during the drying of the shaped particles. Reduction during the step of drying or during a subsequent step may advantageously be effected by using a gaseous reducing agent. The gaseous reducing agent may be, for example, hydrogen or an olefin, such as ethylene or propylene. Reduction may be effected during an initial stage of an olefin epoxidation process when the shaped catalyst is contacted with the feed comprising the olefin.

Suitable cationic silver compounds are, for example, nitrates, acetates, carbonates, citrates, oxalates, lactates

of cationic silver as such or as an amine complex. Suitable complexes of amines may be based on a mono-amine, but preferably they are based on a diamine, in particular a vicinal diamine. Examples of mono-amines are 2-ethanolamine and 2-propanolamine. Examples of diamines are 1,2-ethylene diamine, 1,2-propylene diamine, 2,3-butylene diamine. A preferred cationic silver compound is a silver/1,2-ethylene diamine oxalate complex. The acetates, lactates, citrates and oxalates mentioned in this context enable at least a portion of the cationic silver to be reduced during the drying of the shaped particles. Such complexes and their conversion to metallic silver are known from US-A-4761394, and US-A-4766105, which are incorporated herein by reference.

The dough may comprise, as an additional component, a further element or compound thereof which acts as a promoter when the shaped catalyst is used as an epoxidation catalyst. Eligible further elements may be selected from the group of nitrogen, sulfur, phosphorus, boron, fluorine, Group IA metals, Group IIA metals, rhenium, molybdenum, tungsten, chromium, titanium, hafnium, zirconium, vanadium, thallium, thorium, tantalum, niobium, gallium and germanium and mixtures thereof. Preferably the Group IA metals are selected from lithium, potassium, rubidium and cesium. Most preferably the Group IA metal is lithium, potassium and/or cesium. Preferably the Group IIA metals are selected from calcium and barium. Where possible, the further element may suitably be provided as an oxyanion, for example, as a sulfate, borate, perrhenate, molybdate or nitrate, in salt or acid form.

Preferably, the further element is selected from rhenium, molybdenum, tungsten, and a Group IA metal, which may each be present in a quantity of from 0.01 to 500 mmole/kg, calculated as the element (rhenium, molybdenum,

tungsten or the Group IA metal) on the shaped catalyst. More preferably, the further element is rhenium, in particular together with one or more of tungsten, molybdenum, chromium, sulfur, phosphorus, and boron, and in particular together with a Group IA metal. Compounds of nitrogen may be nitrate- or nitrite-forming compounds, which may be present in a quantity of from 0.01 to 500 mmole/kg, calculated as nitrogen on the shaped catalyst. The nitrate- or nitrite-forming compounds and particular selections of nitrate- or nitrite-forming compounds are as defined hereinafter. The nitrate- or nitrite-forming compound is in particular a Group IA metal nitrate or a Group IA metal nitrite. Again, rhenium, molybdenum, tungsten or the nitrate- or nitrite-forming compound may suitably be provided as an oxyanion, for example as a perrhenate, molybdate, tungstate or nitrate, in salt or acid form.

Preferred amounts of catalytic components of the dough are, when calculated as the element, relative to the weight of the shaped catalyst:

- silver from 10 to 500 g/kg, more preferably from 50 to 500 g/kg, most preferably from 50 to 400 g/kg, in particular from 50 to 250 g/kg,
- rhenium from 0.01 to 50 mmole/kg, if present,
- the rhenium co-promoter (that is a promoter comprising tungsten, molybdenum, chromium, sulfur, phosphorus, boron, as mentioned hereinbefore) each from 0.1 to 30 mmole/kg, if present, and
- the Group IA metal each from 0.1 to 500 mmole/kg, if present.

As used herein, the quantity of Group IA metal present in the catalyst is deemed to be the quantity in so far as it can be extracted from the shaped catalyst with de-ionized water at 100 °C. The extraction method involves extracting a

10-gram sample of the shaped catalyst three times by heating it in 20 ml portions of de-ionized water for 5 minutes at 100 °C and determining in the combined extracts the relevant metals by using a known method, for example atomic absorption spectroscopy.

The dough may comprise a liquid, which will give the dough a consistency suitable for moulding it into the desired shape when using a selected moulding technique. Depending on the selected moulding technique, the quantity of liquid may be for example in the range of from 1 to 70 %w, and typically in the range of from 5 to 60 %w, relative to the total weight of the dough. More typically, the quantity of liquid may be in the range of from 7 to 40 %w, in particular from 10 to 35 %w, relative to the total weight of the dough. Suitable liquids are aqueous liquids, and non-aqueous liquids. Aqueous liquids are suitably water, or a mixture of water and an organic compound, such as, for example, methanol, ethanol, acetone, amine, formaldehyde, or a carbohydrate.

In advantageous embodiments the dough may comprise a carboxylic acid having in its molecular structure at least 2 carbon atoms and typically having at most 8 carbon atoms, in particular at most 6 carbon atoms, more in particular at most 4 carbon atoms. The carboxylic acid may or may not partly or wholly be present in the dough in ionized form, that is in carboxylate form. The carboxylic acid may comprise in its molecular structure a single carboxyl group or a plurality of carboxyl groups, or it may have hydroxy groups, typically one, two or three hydroxyl groups, in addition to one or more carboxyl groups. In particular, the carboxylic acid may comprise in its molecular structure two carboxyl groups. Examples of suitable carboxylic acids are acetic acid, lactic acid, adipic acid, citric acid, maleic acid, malonic acid and succinic acid. A preferred carboxyl acid is oxalic acid.

The presence of such carboxylic acids in the dough is advantageous in that it improves the moulding of the dough into shaped particles, in particular by extrusion. The presence of such carboxylic acids also tends to improve the performance of the catalyst, typically the initial selectivity, in particular when the catalyst is operated at conditions of a relatively low gas hourly space velocity (GHSV), as defined hereinafter, for example lower than 7000 $\text{Nl}/(\text{l.h})$. The quantity of the carboxylic acid present in the dough may be more than 1 %w, for example more than 5 %w, typically at least 8 %w, preferably at least 10 %w, relative to the weight of the support material or precursor thereof. The quantity of the carboxylic acid present in the dough may be at most 25 %w, typically at most 20 %w, preferably at most 15 %w, relative to the weight of the support material or precursor thereof.

In an embodiment, amongst others, a solution comprising a silver diamine complex and a reducing acid may be prepared, for example as taught in US-4766105, and additional promoter components, if any, and further silver component, if any, may be added to the solution, and the mixture so obtained is mixed with the support material or a precursor thereof, to form the dough. Such embodiment has been illustrated in the Examples hereinafter, in the preparation of Catalyst A. In another embodiment, a dry mixture of the solid components of the dough, amongst which the support material or a precursor thereof, may be admixed with a solution of catalyst components, to form the dough. Such other embodiment has been illustrated in the Examples hereinafter, in the preparation of Catalyst D. In a preferred embodiment, amongst others, the silver component and promoter components, if any, may be dissolved or otherwise mixed with at least a portion of the liquid and then combined with the support

material or precursor thereof, to form the dough. In this preferred embodiment a catalyst can be prepared which provides an improved performance, typically in terms of the initial selectivity, in particular when the catalyst is
5 operated at conditions of a relatively low GHSV, as defined hereinbefore. Such preferred embodiment has been illustrated in the Examples hereinafter, in the preparation of Catalysts C, E and F.

The shaped particles may be formed from the dough by any
10 convenient moulding process, such as sieving, spraying, or spray drying, but preferably they are moulded by extrusion, agglomeration or pressing. For applicable methods, reference may be made to, for example, US-A-5145824, US-A-5512530, US-A-5384302, US-A-5100859 and US-A-5733842, which are herein
15 incorporated by reference.

Examples of agglomeration include, but are not limited to, tabletting, briquetting, pelleting, rolling, and tumbling. Methods of pressing include single-action pressing, double-action pressing, roll pressing, multiple
20 pressing, isostatic pressing, hot pressing, as well as other pressing methods known to one skilled in the art. Reference may be made to *Size Enlargement by Agglomeration*, by Wolfgang Pietsch (John Wiley and Sons, 1991), pages 12-18 and 118.

To facilitate such moulding processes, in particular
25 extrusion, the dough may suitably comprise up to about 30 %w and preferably from 2 to 25 %w, based on the weight of the dough, of extrusion aids. Suitable extrusion aids may be for example petroleum jelly, hydrogenated oil, synthetic alcohol, synthetic ester, glycol, polyolefin oxide, polyethylene
30 glycol, or a saturated or unsaturated fatty acid having more than 8 carbon atoms.

The shaped particles may be dried at a temperature below 1000 °C, preferably at a temperature of at most 600 °C, more

preferably at most 550 °C, in particular at most 500 °C.

Typically, drying may take place at a temperature of at least 50 °C, more typically at least 250 °C, in particular at least 300 °C. Typically drying is carried out for a period of up to 100 hours and preferably for from 5 minutes to 50 hours. Drying may be carried out in any atmosphere, such as in air, nitrogen, or helium, or mixtures thereof. Drying may also be carried out in a reducing atmosphere, enabling reduction of cationic silver as described hereinbefore. Preferably, in particular when the shaped particles contain organic material, the drying is at least in part or entirely carried out in an oxidizing atmosphere, such as for example in air or in another oxygen containing atmosphere.

In particular when the drying is performed at a temperature of at least 50 °C, more typically at least 250 °C, in particular at least 300 °C, and at a temperature of at most 600 °C, more typically at most 550 °C, in particular at most 500 °C, a mechanically stronger shaped catalyst is obtained, as can be found by attrition and/or crush strength tests. Also, when using the catalyst so obtained in an epoxidation process, a more rapid start-up of the epoxidation process may be accomplished, which means that the initial selectivity may be reached at a lower cumulative olefin oxide production, and substantially without detriment to other performance properties, for example initial activity, initial selectivity, activity stability and selectivity stability.

The attrition test as referred to herein is in accordance with ASTM D4058-96, wherein the test sample is tested as such after its preparation, that is with elimination of Step 6.4 of the said method, which represents a step of drying the test sample. The attrition measured for the shaped catalyst in accordance to the invention is

typically at most 50 %, preferably at most 40 %, in particular at most 30 %. Frequently, the attrition is at least 10 %, in particular at least 15 %, and more in particular at least 20 %.

5 The crush strength as referred herein is as measured in accordance with ASTM D6175-98, wherein the test sample is tested as such after its preparation, that is with elimination of Step 7.2 of the said method, which represents a step of drying the test sample. The crush strength of the
10 shaped catalyst in accordance with the invention, in particular when measured as the crush strength of hollow cylindrical particles of 8.8 mm external diameter and 3.5 mm internal diameter, is typically at least 2 N/mm, preferably at least 4 N/mm, and in particular at least 6 N/mm. The
15 crush strength, in particular when measured as the crush strength of hollow cylindrical particles of 8.8 mm external diameter and 3.5 mm internal diameter, is frequently at most 25 N/mm, in particular at most 20 N/mm, and more in particular at most 15 N/mm. When the shaped catalyst is
20 present as shaped particles of a certain shape other than the particular hollow cylinders as defined, the crush strength of the shaped catalyst being present as the particular hollow cylinders is measured by repeating the preparation of the catalyst with the difference that the dough is moulded into
25 shaped particles which are the particular hollow cylinders, instead of moulding into the shaped particles of the certain shape, and the crush strength of the hollow cylinders obtained is measured. The catalyst particles having the shape of the particular hollow cylinder have a cylindrical
30 bore, defined by the internal diameter, which is co-axial with the external cylinder. Such catalyst particles, when they have a length of about 8 mm, are frequently referred to as "nominal 8 mm cylinders", or "standard 8 mm cylinders".

The shape and size of the shaped particles is in general determined by the needs of an epoxidation process and the dimensions of an epoxidation reactor in which they are to be deposited. Generally, it is found very convenient to use

5 shaped particles in the form of, for example, trapezoidal bodies, cylinders, saddles, spheres, doughnuts. The shaped particles may typically have a largest outer dimension in the range of from 3 to 15 mm, preferably from 5 to 10 mm. They may be solid or hollow, that is they may have a bore.

10 Cylinders may be solid or hollow, and they may have a length typically from 3 to 15 mm, more typically from 5 to 10 mm, and they may have a cross-sectional, outer diameter typically from 3 to 15 mm, more typically from 5 to 10 mm. The ratio of the length to the cross-sectional diameter of the

15 cylinders may typically be in the range of from 0.5 to 2, more typically from 0.8 to 1.25. The shaped particles, in particular the cylinders, may be hollow, having a bore typically having a diameter in the range of from 0.1 to 5 mm, preferably from 0.2 to 2 mm. The presence of a relatively

20 small bore in the shaped particles increases their crush strength and the achievable packing density, relative to the situation where the particles have a relatively large bore. The presence of a relatively small bore in the shaped particles is beneficial in the drying of the shaped catalyst,

25 relative to the situation where the particles are solid particles, that is having no bore.

If desired, further materials may be deposited onto the shaped catalyst, for example by impregnation or by coating, in order to further enhance its performance. However, this

30 is normally not a preferred embodiment, as it renders the preparation of the shaped catalyst more complicated. It is preferred that all such further materials are included in the dough before it is moulded into shaped particles.

Although the epoxidation process may be carried out in many ways, it is preferred to carry it out as a gas phase process, i.e. a process in which the feed is contacted in the gas phase with the shaped catalyst which is present as a solid material, typically in a packed bed. Generally the process is carried out as a continuous process.

The olefin for use in the present epoxidation process may be any olefin, such as an aromatic olefin, for example styrene, or a di-olefin, whether conjugated or not, for example 1,9-decadiene or 1,3-butadiene. Mixtures of olefins may be used. Typically, the olefin is a monoolefin, for example 2-butene or isobutene. Preferably, the olefin is a mono- α -olefin, for example 1-butene or propylene. The most preferred olefin is ethylene.

The olefin concentration in the feed may be selected within a wide range. Typically, the olefin concentration in the feed will be at most 80 mole%, relative to the total feed. Preferably, it will be in the range of from 0.5 to 70 mole%, in particular from 1 to 60 mole%, on the same basis. As used herein, the feed is considered to be the composition which is contacted with the shaped catalyst.

The epoxidation process may be air-based or oxygen-based, see "Kirk-Othmer Encyclopedia of Chemical Technology", 3rd edition, Volume 9, 1980, pp. 445-447. In the air-based process air or air enriched with oxygen is employed as the source of the oxidizing agent while in the oxygen-based processes high-purity (at least 95 mole%) oxygen is employed as the source of the oxidizing agent. Presently most epoxidation plants are oxygen-based and this is a preferred embodiment of the present invention.

The oxygen concentration in the feed may be selected within a wide range. However, in practice, oxygen is generally applied at a concentration which avoids the

flammable regime. Typically, the concentration of oxygen applied will be within the range of from 1 to 15 mole%, more typically from 2 to 12 mole% of the total feed.

5 In order to remain outside the flammable regime, the concentration of oxygen in the feed may be lowered as the concentration of the olefin is increased. The actual safe operating ranges depend, along with the feed composition, also on the reaction conditions such as the reaction temperature and the pressure.

10 A reaction modifier may be present in the feed for increasing the selectively, suppressing the undesirable oxidation of olefin or olefin oxide to carbon dioxide and water, relative to the desired formation of olefin oxide. Many organic compounds, especially organic halides and
15 organic nitrogen compounds, may be employed as the reaction modifier. Nitrogen oxides, hydrazine, hydroxylamine or ammonia may be employed as well. It is frequently considered that under the operating conditions of olefin epoxidation the nitrogen containing reaction modifiers are precursors of
20 nitrates or nitrites, i.e. they are so-called nitrate- or nitrite-forming compounds (cf. e.g. EP-A-3642 and US-A-4822900, which are incorporated herein by reference).

Organic halides are the preferred reaction modifiers, in particular organic bromides, and more in particular organic
25 chlorides. Preferred organic halides are chlorohydrocarbons or bromohydrocarbons. More preferably they are selected from the group of methyl chloride, ethyl chloride, ethylene dichloride, ethylene dibromide, vinyl chloride or a mixture thereof. Most preferred reaction modifiers are ethyl
30 chloride and ethylene dichloride.

Suitable nitrogen oxides are of the general formula NO_x wherein x is in the range of from 1 to 2, and include for example NO, N_2O_3 and N_2O_4 . Suitable organic nitrogen

compounds are nitro compounds, nitroso compounds, amines, nitrates and nitrites, for example nitromethane, 1-nitropropane or 2-nitropropane. In preferred embodiments, nitrate- or nitrite-forming compounds, e.g. nitrogen oxides
5 and/or organic nitrogen compounds, are used together with an organic halide, in particular an organic chloride.

The reaction modifiers are generally effective when used in low concentration in the feed, for example up to 0.1 mole%, relative to the total feed, for example from
10 0.01×10^{-4} to 0.01 mole%. In particular when the olefin is ethylene, it is preferred that the reaction modifier is present in the feed at a concentration of from 0.1×10^{-4} to 50×10^{-4} mole%, in particular from 0.3×10^{-4} to 30×10^{-4} mole%, relative to the total feed.

15 In addition to the olefin, oxygen and the reaction modifier, the feed may contain one or more optional components, such as carbon dioxide, inert gases and saturated hydrocarbons. Carbon dioxide is a by-product in the epoxidation process. However, carbon dioxide generally has
20 an adverse effect on the catalyst activity. Typically, a concentration of carbon dioxide in the feed in excess of 25 mole%, preferably in excess of 10 mole%, relative to the total feed, is avoided. A concentration of carbon dioxide as low as 1 mole% or lower, relative to the total feed, may be
25 employed. Inert gases, for example nitrogen or argon, may be present in the feed in a concentration of from 30 to 90 mole%, typically from 40 to 80 mole%. Suitable saturated hydrocarbons are methane and ethane. If saturated
hydrocarbons are present, they may be present in a quantity
30 of up to 80 mole%, relative to the total feed, in particular up to 75 mole%. Frequently they are present in a quantity of at least 30 mole%, more frequently at least 40 mole%.

Saturated hydrocarbons may be added to the feed in order to increase the oxygen flammability limit.

The epoxidation process may be carried out using reaction temperatures selected from a wide range. Preferably
5 the reaction temperature is in the range of from 150 to 325 °C, more preferably in the range of from 180 to 300 °C.

The epoxidation process is preferably carried out at a reactor inlet pressure in the range of from 1000 to 3500 kPa. Gas hourly space velocity ("GHSV") is the unit volume of gas
10 at normal temperature and pressure (0 °C, 1 atm, i.e. 101.3 kPa) passing over one unit volume of packed catalyst per hour. Preferably, when the epoxidation process is as a gas phase process involving a packed bed of the shaped catalyst particles, the GHSV may be in the range of from 1200 to 12000
15 Nl/(l.h), and, more preferably, GSHV is in the range of from 1500 to less than 10000 Nl/(l.h). Preferably, the process is carried out at a work rate in the range of from 0.5 to 10 kmole olefin oxide produced per m³ of catalyst per hour, in particular 0.7 to 8 kmole olefin oxide produced per m³ of
20 catalyst per hour. As used herein, the work rate is the amount of the olefin oxide produced per unit volume of the packed bed of the shaped catalyst particles per hour and the selectivity is the molar quantity of the olefin oxide formed relative to the molar quantity of the olefin converted.

25 The olefin oxide produced may be recovered from the reaction mixture by using methods known in the art, for example by absorbing the olefin oxide from a reactor outlet stream in water and optionally recovering the olefin oxide from the aqueous solution by distillation. At least a
30 portion of the aqueous solution containing the olefin oxide may be applied in a subsequent process for converting the olefin oxide into a 1,2-diol or a 1,2-diol ether.

The olefin oxide produced in the epoxidation process may be converted into a 1,2-diol, a 1,2-diol ether, or an alkanolamine. As this invention leads to a more attractive process for the production of the olefin oxide, it
5 concurrently leads to a more attractive process which comprises producing the olefin oxide in accordance with the invention and the subsequent use of the obtained olefin oxide in the manufacture of the 1,2-diol, 1,2-diol ether, and/or alkanolamine.

10 The conversion into the 1,2-diol or the 1,2-diol ether may comprise, for example, reacting the olefin oxide with water, suitably using an acidic or a basic catalyst. For example, for making predominantly the 1,2-diol and less 1,2-diol ether, the olefin oxide may be reacted with a ten fold
15 molar excess of water, in a liquid phase reaction in presence of an acid catalyst, e.g. 0.5-1.0 %w sulfuric acid, based on the total reaction mixture, at 50-70 °C at 1 bar absolute, or in a gas phase reaction at 130-240 °C and 20-40 bar absolute, preferably in the absence of a catalyst. If the proportion
20 of water is lowered the proportion of 1,2-diol ethers in the reaction mixture is increased. The 1,2-diol ethers thus produced may be a di-ether, tri-ether, tetra-ether or a subsequent ether. Alternative 1,2-diol ethers may be prepared by converting the olefin oxide with an alcohol, in
25 particular a primary alcohol, such as methanol or ethanol, by replacing at least a portion of the water by the alcohol.

The conversion into the alkanolamine may comprise, for example, reacting the olefin oxide with ammonia. Anhydrous or aqueous ammonia may be used, although anhydrous ammonia is
30 typically used to favour the production of monoalkanolamine. For methods applicable in the conversion of the olefin oxide into the alkanolamine, reference may be made to, for example US-A-4845296, which is incorporated herein by reference.

The 1,2-diol and the 1,2-diol ether may be used in a large variety of industrial applications, for example in the fields of food, beverages, tobacco, cosmetics, thermoplastic polymers, curable resin systems, detergents, heat transfer systems, etc. The alkanolamine may be used, for example, in the treating ("sweetening") of natural gas.

Unless specified otherwise, the low-molecular weight organic compounds mentioned herein, for example the olefins, 1,2-diols, 1,2-diol ethers, alkanolamines and reaction modifiers, have typically at most 40 carbon atoms, more typically at most 20 carbon atoms, in particular at most 10 carbon atoms, more in particular at most 6 carbon atoms. As defined herein, ranges for numbers of carbon atoms (i.e. carbon number) include the numbers specified for the limits of the ranges.

Having generally described the invention, a further understanding may be obtained by reference to the following examples, which are provided for purposes of illustration only and are not intended to be limiting unless otherwise specified.

EXAMPLES

Shaped Catalysts A, B, C and D comprising 20 %w silver, 3 mmole rhenium/kg, 1.5 mmole tungsten/kg, 20 mmole lithium/kg and 3.4 mmole cesium/kg, based on the weight of the catalyst, were prepared as follows.

A silver-1,2-ethylene diamine-oxalate stock solution was prepared by using the procedure outlined in US-A-4766105, column 17, line 50 - column 18, line 25, which is incorporated herein by reference. The resulting solution contained approximately 30 %w silver.

Silver oxide and subsequently a solution of ammonium perrhenate, ammonium metatungstate, cesium hydroxide and lithium hydroxide in a small volume of water were added to a

40 ml sample of the stock solution. The resulting slurry was added to 120 g of an α -alumina powder (obtained from ALCOA/ALMATIS (Ludwigshafen, Germany), type CL2500 SG), to form a dough. The dough contained about 24 %w liquid,
5 relative to the weight of the dough. The quantities of silver oxide, ammonium perrhenate, ammonium metatungstate, cesium hydroxide and lithium hydroxide were such that the shaped catalyst had a composition as specified above. This dough was then pressed into tablets of 30 mm diameter and 2
10 mm thickness. The tablets were dried at 250 °C, for 10 minutes in air, to provide "Catalyst A", in accordance with the invention.

For comparative purposes, a shaped carrier was prepared by extruding a dough based on the same α -alumina as employed
15 in the preparation of Catalyst A into shaped particles. A catalyst was then prepared by impregnating the shaped particles with a sample of the above silver stock solution and promoter solution, and drying the impregnated carrier at 250 °C, for 6 minutes in air, to provide Catalyst B, not in
20 accordance with the invention. The quantities of silver solution, ammonium perrhenate, ammonium metatungstate, cesium hydroxide and lithium hydroxide were such that the shaped catalyst had a composition as specified above.

Catalyst C was prepared as follows. Silver oxide
25 (1075 g) and subsequently 420 g of oxalic acid were mixed into 600 g of a 1,2-ethylene diamine/water mixture (1/1 by weight). Thereafter, a solution of ammonium perrhenate, ammonium metatungstate and lithium hydroxide in 200 ml of water was added, followed by adding a solution of cesium
30 hydroxide in water. The slurry so obtained was added to 4 kg of an α -alumina powder (obtained from ALCOA/ALMATIS (Ludwigshafen, Germany), type CL2500 SG) and mixed in a muller for 20 minutes to obtain a dough. A small amount of

water was added to obtain a consistency of the dough which is suitable for extrusion. The dough was extruded into hollow cylinders and then dried at 95 °C for one hour and subsequently at 500 °C for one hour, to provide Catalyst C, in accordance with the invention. The quantities of silver oxide, ammonium perrhenate, ammonium metatungstate, cesium hydroxide and lithium hydroxide were such that the shaped catalyst had a composition as specified above. The hollow cylinders had dimensions as follows: 10 mm outside diameter, 4 mm inside diameter and 10 mm height.

Catalyst D was prepared as follows. Silver oxide (8.06 g), 30 g of an α -alumina powder (obtained from ALCOA/ALMATIS (Ludwigshafen, Germany), type CL2500 SG) and 3.13 g of oxalic acid were dry mixed. Separately, ammonium perrhenate, ammonium metatungstate and lithium hydroxide were dissolved into 6.9 g of a 1,2-ethylene diamine/water mixture (1/1 by weight), and 0.037 g of a solution of cesium hydroxide in water was added thereto. The resulting solution was then mixed into the dry mixture of silver oxide, α -alumina powder and oxalic acid and a dough was formed by mulling in a muller. A small amount of water was added to obtain a consistency of the dough which is suitable for pressing. Then the dough was pressed into tablets of 30 mm diameter and 2 mm thickness. The tablets were then dried at 250 °C, for 5 minutes in air, to provide Catalyst D, in accordance with this invention. The quantities of silver oxide, ammonium perrhenate, ammonium metatungstate, cesium hydroxide and lithium hydroxide were such that the shaped catalyst had a composition as specified above.

Catalyst E, according to the invention, comprising 20 %w silver, 3.25 mmole rhenium/kg, 2.5 mmole tungsten/kg, 20 mmole lithium/kg and 6.0 mmole cesium/kg, based on the weight of the catalyst, was prepared in a manner similar as

Catalyst C, but with the following differences:

- the catalyst preparation was performed at a scale which required using 35 g of α -alumina powder,
- for the preparation of Catalyst E an α -alumina powder was
5 obtained from ALTECH/ALCAN INC. (Gardanne, France), type P122B,
- the quantity of oxalic acid was 4.0 g,
- the dough was pressed into tablets of 30 mm diameter and 2 mm thickness, and
- 10 - drying was performed at 400 °C for one hour.

Catalyst F, according to the invention, was prepared in a similar manner as Catalyst E, but with the following difference:

- the formulation comprised 20 %w silver, 3.25 mmole
15 rhenium/kg, 2.0 mmole tungsten/kg, 20 mmole lithium/kg and 5.8 mmole cesium/kg, based on the weight of the catalyst.

The catalysts were used to produce ethylene oxide from ethylene and oxygen. To do this, 1.7 g crushed samples of Catalysts A-D (20-30 mesh, or 0.59 to 0.84 mm) each were
20 loaded into a 3.86 mm inside diameter stainless steel U-shaped tube. The tubes were immersed in a molten metal bath (heat medium) and the ends were connected to a gas flow system. The inlet gas flow rates were 0.28 Nl/minute. The inlet gas pressure was 1450 kPa.

25 The gas mixture passed through the catalyst beds, in a "once-through" operation, during the entire test run including the start-up, consisted of 30 %v ethylene, 8 %v oxygen, 5 %v carbon dioxide, 57 %v nitrogen and 2.0 to 6.0 ppmv ethyl chloride.

30 The initial reactor temperature was 180 °C and this was ramped up at a rate of 10 °C per hour to 225 °C and then adjusted so as to achieve a constant ethylene oxide content of 1.5 %v in the outlet gas stream, whilst the ethyl chloride

concentration was adjusted from time to time as to provide and maintain an optimum selectivity of the formation of ethylene oxide. Performance data at this conversion level are usually obtained when the catalyst has been on stream for
5 a total of at least 1-2 days. Subsequently, for Catalysts A and Catalyst B, the testing was continued by adjusting the temperature, whenever needed so as to maintain a constant ethylene oxide content of 1.5 %v in the outlet gas stream.

Catalysts E and F were used in a similar manner as
10 Catalysts C and D, but with the following differences:
- the sample size of crushed catalyst (14-20 mesh, or 0.84 to 1.4 mm) was 4 g,
- the inside diameter of the tube was 4.57 mm, and
- the ethylene oxide content in the outlet gas stream was
15 3.1 %v.

The initial performance values for selectivity and temperature of each of the catalysts are reported in Table I, below. Table I also provides for Catalysts A, B, E, and F the performance values after a cumulative production of
20 0.5 kTon ethylene oxide per m³ of catalyst bed was achieved. Table I additionally provides for Catalysts A, E, and F the performance values after a cumulative production of 1.0 kTon ethylene oxide per m³ of catalyst bed was achieved. A lower temperature needed to accomplish a certain ethylene oxide
25 content in the outlet gas stream is indicative for a higher activity of the catalyst.

TABLE I

Catalyst	A *)	B **)	C *)	D *)	E *)	F *)
Initial selectivity, mole%	88.5	87.3	88	86	87.7	87.7
Initial activity, °C	251	245	263	249	252	252
Selectivity after 0.5 kTon/m ³ , mole%	88.2	86.6	Not tested	Not tested	87.3	87.7
Temperature after 0.5 kTon/m ³ , °C	258	268	Not tested	Not tested	260	257
Selectivity after 1.0 kTon/m ³ , mole%	87.2	Not tested	Not tested	Not tested	84.0	86.7
Temperature after 1.0 kTon/m ³ , °C	264	Not tested	Not tested	Not tested	278	267
*) invention						
**) comparative						

The data provided in Table I illustrate that in accordance with this invention shaped catalysts can be made which are superior in initial selectivity, activity stability and selectivity stability.

C L A I M S

1. A method of preparing a shaped catalyst, which method comprises moulding a dough into shaped particles and drying at least a portion of the shaped particles at a temperature below 1000 °C, wherein the dough comprises a support material, or a precursor thereof, a silver component, and a further element or compound thereof which acts as a promoter when the shaped catalyst is used as an epoxidation catalyst.
2. A method as claimed in claim 1, wherein the drying of at least a portion of the shaped particles is carried out at a temperature in the range of from 250 to 550 °C, in particular from 300 to 500 °C.
3. A method as claimed in claims 1 or 2, wherein the dough comprises, in addition, more than 1 %w, relative to the weight of the support material or precursor thereof, of a carboxylic acid having in its molecular structure at least 2 carbon atoms.
4. A method as claimed in claim 3, wherein the carboxylic acid having at least 2 carbon atoms comprises in its molecular structure a plurality of carboxyl groups or, in addition to one or more carboxyl groups, one or more hydroxyl groups.
5. A method as claimed in claims 3 or 4, wherein the dough comprises the carboxylic acid in a quantity in the range of from 8 to 20 %w, relative to the weight of the support material or precursor thereof.
6. A method as claimed in any of claims 1-5, wherein the support material, or a precursor thereof, has been treated to reduce its sodium solubilization rate or to decrease its content of water soluble silicates.

7. A method as claimed in any of claims 1-6, wherein the support material, or a precursor thereof, has been water washed.
8. A method as claimed in any of claims 1-7, wherein a liquid comprising the silver component is combined with the support material or precursor thereof to form the dough.
9. A method as claimed in any of claims 1-8, wherein the support material is an α -alumina, or a precursor thereof.
10. A method as claimed in claim 9, wherein the α -alumina is of a platelet structure.
11. A method as claimed in any of claims 1-10, wherein the further element is selected from the group of nitrogen, sulfur, phosphorus, boron, fluorine, Group IA metals, Group IIA metals, rhenium, molybdenum, tungsten, chromium, titanium, hafnium, zirconium, vanadium, thallium, thorium, tantalum, niobium, gallium, germanium and mixtures thereof.
12. A method as claimed in any of claims 1-11, wherein the further element or compound thereof is selected from the group of rhenium, molybdenum, tungsten, Group IA metals, nitrate- or nitrite-forming compounds, and mixtures thereof.
13. A shaped catalyst which is obtainable by a method which comprises moulding a dough into shaped particles and drying at least a portion of the shaped particles at a temperature below 1000 °C, wherein the dough comprises a support material, or a precursor thereof, a silver component, and a further element or compound thereof which acts as a promoter when the shaped catalyst is used as an epoxidation catalyst.

14. A shaped catalyst as claimed in claim 13, wherein the shaped catalyst has an attrition of at most 50 %, in particular at most 40 %, more in particular at most 30 %.

15. A shaped catalyst as claimed in claims 13 or 14, wherein the shaped catalyst has a crush strength of at least 2 N/mm, in particular at least 4 N/mm, more in particular at least 6 N/mm.

16. A shaped catalyst as claimed in any of claims 13-15, wherein the shaped catalyst has a crush strength of at least 2 N/mm, in particular at least 4 N/mm, more in particular at least 6 N/mm, when measured as the crush strength of hollow cylindrical particles having an external diameter of 8.8 mm and an internal diameter of 3.5 mm.

17. A process for the epoxidation of an olefin, which process comprises contacting a feed comprising the olefin and oxygen with a shaped catalyst which is obtainable by a method which comprises moulding a dough into shaped particles and drying at least a portion of the shaped particles at a temperature below 1000 °C, wherein the dough comprises a support material, or a precursor thereof, a silver component, and a further element or compound thereof which acts as a promoter when the shaped catalyst is used as an epoxidation catalyst.

18. A method of using ethylene oxide for making a 1,2-diol, a 1,2-diol ether or an alkanolamine comprising converting an olefin oxide into the 1,2-diol, the 1,2-diol ether, or the alkanolamine, wherein the olefin oxide has been obtained by a process for the epoxidation of an olefin as claimed in claim 17.

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(71) Applicant (for all designated States except US): **SHELL OIL COMPANY** [US/US]; One Shell Plaza, P.O. Box 2463, Houston, TX 77252-2463 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **DUONG, Dien, Hien** [US/US]; 16210 Canario, Houston, TX 77083 (US). **LU, Jian** [US/US]; 14211 Highcroft Avenue, Houston, TX 77077 (US). **VI, Nga, Thihuyen** [US/US]; 20731 Lariat Canyon Drive, Katy, TX 77450 (US).

(74) Agent: **LEMUTH, Richard, F.**; SHELL OIL COMPANY, One Shell Plaza, P.O. Box 2463, Houston, TX 77252-2463 (US).

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(54) Title: A METHOD OF PREPARING A SHAPED CATALYST, THE CATALYST, AND USE OF THE CATALYST

(57) Abstract: A method of preparing a shaped catalyst, which method comprises moulding a dough into shaped particles and drying at least a portion of the shaped particles at a temperature below 1000°C, wherein the dough comprises a support material, or a precursor thereof, and a silver component; the shaped catalyst, and a use of the shaped catalyst.



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INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
B01J23/50 B01J23/68 C07D301/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01J C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CA 1 282 772 C (UNION CARBIDE CORPORATION) 9 April 1991 (1991-04-09) example 20	1-17
X	WO 2004/039496 A (SHELL OIL COMPANY; RUBINSTEIN, LEONID, ISAAKOVICH; GUTIERREZ, CANDIDO) 13 May 2004 (2004-05-13) page 5, line 8 - page 6, line 21	1-8, 11-17
X	WO 2004/030813 A (SHELL OIL COMPANY; RUBINSTEIN, LEONID, ISAAKOVICH; GUTIERREZ, CANDIDO) 15 April 2004 (2004-04-15) page 5, line 10 - line 23	1-8, 11-17
X	US 4 320 031 A (PARTHASARATHY ET AL) 16 March 1982 (1982-03-16) column 2, line 34 - line 44 column 2, line 49 - line 54	1,9
	-/--	

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
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"&" document member of the same patent family

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Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Veefkind, V

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2005/028437

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 299 735 A (MEIN ET AL) 10 November 1981 (1981-11-10) examples IX, VII	1, 9, 10
A	----- EP 0 425 020 A (UNION CARBIDE CHEMICALS AND PLASTICS COMPANY, INC) 2 May 1991 (1991-05-02) the whole document -----	1-17

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2005/028437

Box II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-17

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-17

Process of preparing a shaped catalyst, shaped catalyst and process for the epoxidation of an olefin.

2. claim: 18

Method of using ethylene oxide

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2005/028437

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CA 1282772	C	09-04-1991	NONE
WO 2004039496	A	13-05-2004	AU 2003284183 A1 25-05-2004
			CA 2503954 A1 13-05-2004
			CN 1713957 A 28-12-2005
			EP 1562701 A1 17-08-2005
WO 2004030813	A	15-04-2004	AU 2003278999 A1 23-04-2004
			CA 2500238 A1 15-04-2004
			CN 1684764 A 19-10-2005
			EP 1545768 A1 29-06-2005
US 4320031	A	16-03-1982	NONE
US 4299735	A	10-11-1981	NONE
EP 0425020	A	02-05-1991	AT 176907 T 15-03-1999
			AU 5036793 A 13-01-1994
			AU 639946 B2 12-08-1993
			AU 6466690 A 26-04-1991
			BR 9005240 A 17-09-1991
			CA 2027868 A1 19-04-1991
			DE 69032957 D1 01-04-1999
			DE 69032957 T2 12-08-1999
			DK 425020 T3 27-09-1999
			JP 3030512 B2 10-04-2000
			JP 3207447 A 10-09-1991
			KR 9612093 B1 12-09-1996
			US 5187140 A 16-02-1993